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Conformation of Cyclotriveratrylene by Nuclear Magnetic Resonance Measurements

by

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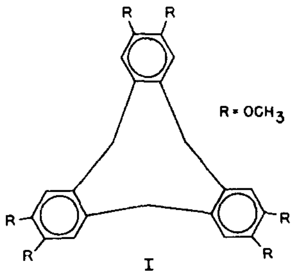
Recently Lindsey[1] established through molecular weight measurements (freezing point depression, vapor pressure osmometry) that the major crystalline product (m.p. 234°C) of veratrole and formaldehyde-hydrochloric acid condensation is cyclotriveratrylene (I) rather than the previously assumed 2,3,6,7-tetramethoxy-9,10-dihydroanthracene[2] or the cyclic hexamer $(C_6H_{10}O_2)_6$.[3] Molecular models favor[1] a crown conformation of the cyclononatriene ring in which the methylene carbons form the truncated apex of a 3-sided pyramidal structure.



I

Nuclear magnetic resonance measurements of the present work confirm the proposed crown conformation and indicate its stability to thermal inversion or interconversion to less symmetrical forms at temperatures to at least 200°C.

Reaction of veratrole with 25% excess paraformaldehyde in 6M HCl at reflux gave I in good yield. Crystallizations from ethanol and CCl_4 gave colorless needles, m.p. 232-234°C; calculations for $(C_6H_{10}O_2)_n$ 72.0% C, 6.73% H, 21.3% O, found 72.08% C, 6.80% H, 21.0% O. The trimeric structure of Lindsey was confirmed by the mass spectrum* which indicated the molecular ion at m/e 450. The loss of one methoxyl gives the second most prominent peak followed in intensity by m/e 299 and 151, corresponding to $(C_9H_{10}O_2)_n = 2,1$ fragments.

The n.m.r. trace in hexachloroacetone solution at 40°C (Fig. 1) shows single peaks at $\tau = 3.06$ (aromatic H) and $\tau = 6.22$ (methoxyl H) and an AB quartet with doublets at $\tau = 6.35$ and $\tau = 5.30$, each split by 14 cps (methylene H). Integration confirms the 1:3:1 ratio of aromatic H:methoxyl H:methylene H. Three signals in deuterated chloroform at room temperature without details of structure are also reported by Cookson in reference (1b).

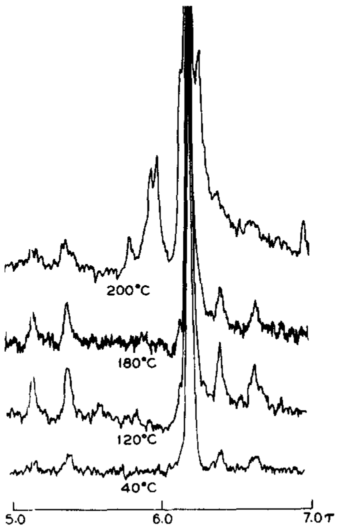


Fig. 1

An AB methylene quartet is entirely consistent with a rigid crown form with three exactly equivalent pairs of axial and equatorial hydrogens. This quartet is retained (Fig. 1) in hexachloroacetone solution to 200 °C where decomposition or reaction occurs as evidenced by appearance of further structure in the spectrum. The calculated relative chemical shift, $\nu_o\ \delta$, is 74 cps ($\delta = \sigma_B - \sigma_A$) and the measured splitting between the doublets is 75 cps, nearly AX behavior.

For the parent ring system, cis-cis-cis-1,4,7-cyclononatriene[4,5,6] at low temperatures (< -25°C) two groups of methylene protons appear corresponding to the non-interconverting crown conformation. These signals coalesce readily above ambient temperatures to a single intermediate peak. The loss of identity of the protons is attributed to averaging of the mirror forms of the crown through a half-crown intermediate whose six conformations are readily interconvertible.[6] Untch and Kurland[4] favor a planar transition state (ammonia-like inversion on the basis of a large negative entropy change. Replacement of the double bonds in cyclononatriene by 1,2 benzene ring derivatives renders crown to crown interconversion, by either sequential or simultaneous rotation processes to average the methylene hydrogens, so unfavorable as not to be seen at temperatures within 30 °C of the melting point.

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* Mass spectrum provided by D. S. Baugher, Petroleum Analytical Research Corp., Houston, Texas; 21-103C C.E.C. instrument operated at vapor temperature of 350 °C.